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Temporal effect of MgO reactivity on the stabilization of lead contaminated soil

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ABSTRACT

Elevated soil lead (Pb) concentrations are a global concern owing to the toxic effects of this heavy metal. Solidification/stabilization (S/S) of soils using reagents like Portland cement (PC) is a common approach for the remediation of Pb contaminated sites. However, it has been reported that under long-term field conditions, the performance of PC treatments can diminish significantly. Therefore, novel reagents that provide longer-term stabilization performance are needed. In this study, four magnesium oxide (MgO) products of different reactivity values were applied (5 wt%) to a Pb contaminated clayey soil. The short-term (1–49 days) and long-term (25–100 years) temporal stabilization effects were investigated by laboratory incubation and accelerated ageing methods, respectively. The concentration of Pb in Toxicity Characterization Leaching Procedure (TCLP) leachate was ~14 mg/L for the untreated soil; ~1.8 times higher than the TCLP regulatory level (5 mg/L). Only one day after treatment with MgO, the leachate concentration was reduced to below the regulatory level (a reduction of 69.4%–83.2%), regardless of the MgO type applied. However, in the long-term accelerated ageing experiments, only treatments using the most reactive MgO type could provide leachate concentrations that were consistently below the TCLP threshold throughout the 100 years of simulated ageing. The soil treated with the MgO of lowest reactivity was the first to exceed the regulatory level, at simulated year 75. It is thus demonstrated that MgO reactivity has a significant effect on its long-term effectiveness for contaminated soil stabilization. This is attributed to differences in their specific surface area and readiness to carbonate, which may facilitate the immobilization of Pb in the long term. It is also noteworthy that compared to PC, reactive MgO is more environmentally friendly owing to lower energy consumption and reduced CO₂ emissions during its manufacture.

1. Introduction

Soil pollution is a pervasive global threat to human health and the environment (Jia et al., 2019; Rai et al., 2019; Wang et al., 2019b). In China, a national soil survey found that 16.1% of the surveyed land exceeded national standards, with the majority of elevated samples (83%) being affected by heavy metals (Zhao et al., 2015; O'Connor et al., 2018b; Song et al., 2019). Exposure to the heavy metal lead (Pb) in contaminated soils poses a particularly high risk to young children (Madrigal et al., 2018; O'Connor et al., 2018a; Jin et al., 2019; Zhang et al., 2019), with blood Pb levels being linked to impaired neurological

development (WHO, 2010). Therefore, the development of effective remediation technologies for elevated soil Pb is of great importance.

Solidification/stabilization (S/S) originated in the 1970s for hazardous waste management (Conner and Hoeffner, 1998), and is now the most widely used technology to remediate Pb contaminated sites. By encapsulating and/or immobilizing heavy metals, S/S technology breaks the exposure pathway, thus reducing the health risk (Jin and Al-Tabbaa, 2014b; Wang et al., 2018b). However, despite numerous applications, S/S long-term effectiveness remains a concern (Wang et al., 2014). It has been discovered that the effectiveness of ordinary Portland cement (PC)-based S/S may diminish under the field ageing processes

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such as acid rainfall, wetting and drying cycles, thawing and freezing cycles, and ultraviolet radiation (Wang et al., 2014; Shen et al., 2018).

In comparison to PC, magnesium oxide (MgO), also known as magnesia, is more resistant to field ageing, having significantly higher durability (Jin and Al-Tabbaa, 2014b; Cao et al., 2018). MgO is typically produced through the thermal decomposition (calcination) of Mg-bearing carbonates such as magnesite and dolomite (Jin and Al-Tabbaa, 2013). This process is considered more environmentally friendly than PC production, because calcination occurs at lower temperature, thus requiring less energy input (Yi et al., 2016). The hydration products of MgO (e.g. brucite, $\text{Mg}(\text{OH})_2$) are much less soluble than those of PC, and they are more resistant to acid rain dissolution, indicating the long-term stability (Jin et al., 2015). Therefore, it is expected that the stabilization of soils with MgO will achieve better long-term effectiveness than with PC. Apart from long-term stability, short-term effectiveness is also critical for practical applications of S/S in site remediation. It is well understood that PC typically takes 28 days to reach sufficient performance (Chen et al., 2009). The effective performance of MgO-based stabilization can potentially be much more rapid. Because the reactivity of MgO can be controlled by adjusting production temperature and residence time, and higher reactive MgO can result in faster hydration and stabilization performance (Jin and Al-Tabbaa, 2013). For instance, Shen et al. (2018) observed that MgO significantly reduced the mobility of Pb in soil after just 1 day.

The hydration of MgO to $\text{Mg}(\text{OH})_2$ plays a vital role in the stabilization process, which immobilizes heavy metals through physical encapsulation, adsorption and precipitation reactions (Shen et al., 2018; Wang et al., 2019a). The hydration kinetics are dependent on the MgO reactivity, which is usually measured by its acid neutralization time (Jin and Al-Tabbaa, 2013). In general, there are three grades of MgO produced through the calcination of magnesite: (i) reactive or light-burnt MgO, which is typically produced at 600–1000 °C; (ii) hard-burnt MgO, which is produced at ~1000–1400 °C and (iii) dead-burnt MgO, produced at above 1400 °C. Numerous studies confirmed the effect of calcination temperature and residence time on the reactivity of MgO, with lower temperatures and shorter residence times forming MgO of higher reactivity, higher surface area, and lower crystallinity (Shand, 2006). The relationship between the reactivity of MgO and the calcination temperature (for magnesite) is summarized in Fig. S1 and Table S1. It can be seen that MgO with higher reactivity is produced at lower calcination temperatures, which follows an exponential relationship.

Theoretically, highly-reactive MgO could rapidly hydrate and effectively immobilize heavy metals in the very short-term, however, its relatively low crystallinity and high surface area makes it susceptible to acid rain dissolution in the longer term. On the other hand, less reactive MgO should have relatively better long-term and lower short term stability because of its slower dissolution and hydration kinetics. MgO is one of the most promising reagents for contaminated soil stabilization, and if the short-term and long-term performance in heavy metal stabilization can be optimized, its practical application can be significantly benefitted. However, no such investigations have been carried out so far.

In this study, MgO with four different reactivity values were applied to the stabilization of a Pb contaminated clayey soil. The short-term effectiveness from 1 to 49 days after treatment was investigated in a laboratory incubation test. Then the long-term effectiveness to 100 years after treatment was investigated by artificially accelerated ageing. This study aimed to find the optimal application of MgO for Pb stabilization in soils.

2. Materials and methods

2.1. MgO and soil

Four MgO products used in this study were manufactured by the calcination of magnesite. The reactivity values of the four products

Table 1

Properties and composition of the four MgO products.

Product	Reactivity (seconds)	BET surface area (m^2/g)	pH	%				
				MgO	SiO_2	CaO	Fe_2O_3	Al_2O_3
M33	33	47.4	10.6	99.0	0.204	0.248	0.126	0.213
M93	93	27.6	10.5	91.9	3.62	2.71	0.845	0.434
M359	359	11.1	10.5	87.5	4.83	3.98	1.32	1.14
M3322	3322	2.30	10.6	88.3	4.76	3.91	1.41	1.12

were determined by the acidic neutralization method proposed in (Jin and Al-Tabbaa, 2014a). Briefly, 5 g of MgO was added to 400 mL of 0.25 M acetic acid solution containing phenolphthalein as a pH indicator. The time from adding the MgO to the change of the solution color was recorded as 33, 93, 359, and 3322 s for the four products (Table 1). The products are labelled herein as M33, M93, M359, and M3322, with M33 having the highest reactivity. Brunauer–Emmett–Teller (BET) specific surface areas for the MgO products were determined to be 47.4 m^2/g for M33 to 2.30 m^2/g for M3322 (Table 1), which were measured by N_2 adsorption/desorption using a Tristar II 3020 (Micromeritics) instrument. The pH values of all MgO products were similar, at pH 10.5–10.6, which were determined at a solid/liquid ratio of 1:5 g/mL using a pH electrode. The chemical compositions were determined by X-ray fluorescence (XRF) using an APL PerformX analyzer (Thermo Fisher), which showed that the MgO purity generally decreased with decreasing reactivity because more ashes (e.g., SiO_2 and CaO) formed at higher calcination temperatures (Table 1).

The soil treated was a Pb contaminated soil washing residue. Its description and properties can be found in Shen et al. (2018) and in Table 2. The clayey soil has a relatively high pH value of 9.14. The soil was oven dried, ground, and sieved (< 2 mm). The concentration of Pb in the soil was determined after microwave assisted acid digestion (USEPA method 3051) to be 4280 mg/kg by inductively coupled plasma optical emission spectrometer (ICP-OES).

2.2. Short-term incubation

Based on previous studies (Shen et al., 2018), the four MgO products were added to soil at a dosage rate of 5 wt%. Along with a control sample (0% dosage) the soil moisture content was raised to 40% (wt. water to dry soil) and thoroughly mixed. The moisture 40% was selected based on pre-trials at water content of 10–50%, which found that 40% is the most suitable to avoid too dry or too wet for the soil. The soils were incubated in sealed containers at ambient temperature and saturated relative humidity for 49 days. Sub-samples were periodically collected for further analysis on days 1, 7, 28, and 49.

2.3. Long-term ageing

Quantitative accelerated ageing based on wetting-drying cycles was applied to the soils after 49-days incubation according to the procedure

Table 2

Properties of the Pb contaminated soil.

Property	Value
pH	9.14
Clay (0–0.02 mm) (%) ^a	89.7
Silt (0.002–0.05 mm) (%) ^a	10.3
Pb (mg/kg)	4280
Al_2O_3 (%)	12.5
MnO (%)	3.36
CaO (%)	1.44

(a-based on United States Department of Agriculture System)

described in Shen et al. (2018). Rain water dissolution is one of the most important factors that contribute to the mobilization of heavy metals under field conditions. Therefore, carbonic acid (pH 5.6) was used to simulate natural rain water (Du et al., 2017). Assuming 1 m³ of soil (at a dry density of 1.3 g/cm³) receives 2000 mm natural rainfall over an area of 1 m² (Suzuki et al., 2013), then it can be calculated that 1 g of dry soil receives 1.538 mL of rain water annually.

For each wetting-drying cycle, the soils were mixed with carbonic acid solution at the solid (dry weight) to liquid ratio of 1:9.625 g/mL and the mixture was stirred for 8 h, representing 6.25 years of rainfall wash. After stirring, the mixture was settled and the supernatant was removed. The soils were loosely placed on ceramic trays and oven dried at 40 °C to reach constant weight (typically taking around 16 h) to complete the drying process. The soils underwent a total of 16 wetting-drying cycles, with samples collected for analysis after 4, 8, 12, and 16 cycles simulating 25, 50, 75, and 100 years of field ageing.

2.4. Chemical and microstructural analysis

Collected samples were first oven dried at 40 °C to reach constant weight. The pH of the samples was then tested at a solid/liquid ratio of 1:5 g/mL using a pH electrode. The leachability of Pb in the samples were evaluated following US EPA Method 1311 - Toxicity Characteristic Leaching Procedure (TCLP). Briefly, the soil and buffer solution (HOAc/NaOAc, pH 2.88) were mixed at a solid to liquid ratio of 1:20 g/mL in a polyethylene tube, and shaken at 250 rpm for 18 h before filtration. Pb concentrations in the filtrate were measured by ICP-OES. The total metal concentrations in soil samples were determined by ICP-OES after microwave assisted acid digestion (USEPA method 3051). The crystalline phases in the samples were examined using a D8 ADVANCE X-ray diffractometer (XRD) (Bruker). Briefly, dry samples were mounted on a flat holder and examined with a Cu K α source operating at 40 kV and 40 mA, emitting radiation at a wavelength of 1.5406 Å. The scanning regions were between 2 θ values of 10–80° at a step rate of 0.1 s/step and a resolution of 0.01°/step.

The leaching behavior of Pb in the samples was determined by a 4-step sequential extraction procedure (Shen et al., 2016). Briefly, Pb was partitioned into four fractions through the following steps:

F1 – exchangeable fraction: The soils (1 g) was extracted with 8 mL of 0.5 M MgCl₂ (adjusted to pH 7.0 using NaOH or HCl) and shaken at 250 rpm for 20 min at room temperature;

F2 – carbonate-bound fraction: The solid residue from Step 2 was extracted with 8 mL of 1 M NaOAc (adjusted to pH 5.0 with HOAc) and shaken at 250 rpm for 5 h at room temperature;

F3 – reducible fraction: The residue from Step 2 was extracted with 20 mL of 0.04 M NH₂OH·HCl in 25% (v/v) HOAc followed with occasional agitation for 6 h at 96 °C;

F4 – oxidizable and residual fractions: The total Pb concentration in soil determined by microwave digestion subtracted by the sum the fraction 1, 2, and 3.

Following each step, the samples were centrifuged, and the supernatant was filtered (< 0.22 μ m), preserved by acidification, and diluted when necessary before determining the Pb concentration by ICP-OES. The remaining soil was washed with 20 mL deionized water prior to the following extraction step.

2.5. Statistical analysis

All experiments except XRD tests were conducted in duplicate. The mean and standard deviations (SDs) are presented for each experiment. The significance of differences between each group was determined by one-way ANOVA using Duncan method at the significant level of 0.05 using SPSS 17, and is indicated by different lower case letters in the figures.

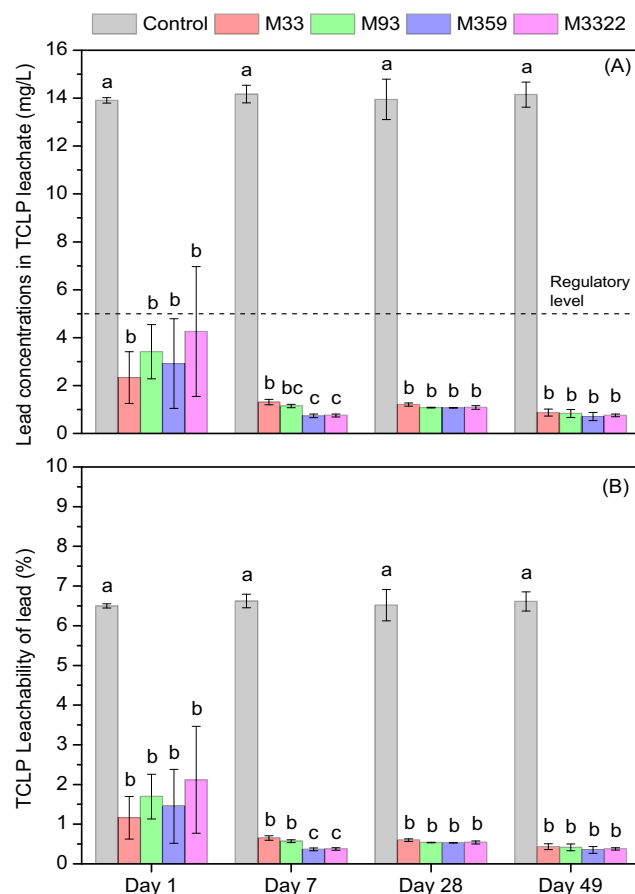


Fig. 1. TCLP leaching of treated soils across 49 days of incubation: (A) Pb leachate concentrations, (B) Pb leachability as a percentage of total Pb.

3. Results and discussion

3.1. Short-term effectiveness

The TCLP leachate Pb concentration of the untreated soil was ~14 mg/L (Fig. 1), which is 1.8 times above the regulatory level (5 mg/L), this suggests that 6.50% of the total Pb in the soil was leachable. After MgO treatment, the TCLP concentrations significantly reduced to below the regulatory level (a reduction of 69.4%–83.2%) only 1 day after treatment, regardless of MgO reactivity; the Pb leachability was reduced to only 1.16%–2.12% of the total Pb. The TCLP concentrations further reduced after seven days of incubation to 0.75–1.31 mg/L, and then remained relatively constant from day 7 to day 49 of incubation.

It is of note that the SDs of the data for M33, M93, M359, and M3322 at Day 1 (Fig. 1) were relatively large, reflecting the MgO hydration being at an early stage, and the distribution within the soil samples having not reached uniformity, resulting in the spatial heterogeneity. By day 7, the SDs significantly reduced, suggesting better distribution and homogeneous MgO hydration.

Table 3 summarizes the time-dependent performance of various MgO based materials for heavy metal stabilization in the published literature. Nzediegwu et al. (2018) also observed rapid immobilization of Pb by MgO, but with the inclusion of Ground Granulated Blast-furnace Slag (GGBS). Jin and Al-Tabbaa (2014b) reported that MgO + GGBS effectively immobilized Pb and Zn by 7 days after treatment, with the TCLP leachate concentrations remaining relatively constant from day 7 to day 28. Other studies have found that the immobilization of heavy metals with MgO was still developing after 28 days (Goodarzi and Movahedrad, 2017; Wang et al., 2018a). The differences in temporal performance may result from differences in soil

Table 3
Temporal performance of MgO-based materials in heavy metal stabilization.

Material	MgO reactivity (s)	Soil contaminant (and concentration as mg/kg)	Dosage (wt%)	Time scale	Time-dependent stabilization	Reference
MgO	33, 93, 359, 3322	Pb (4280)	5	1–49 days	Rapid immobilization at Day 1, gradually developed to Day 7 and then remain relatively constant	Present study
MgO	33, 93, 359, 3322	Pb (4280)	5	Simulated 25–100 years	Immobilization remains effective at Year 75 except M3322, only M33 was effective at Year 100	Present study
MgO	N/A	Zn (1500), Cu (1200), Ni (1600), Pb (2500)	8.4	9–28 days	Development of immobilization from Day 9 to Day 28 after treatment	(Wang et al., 2018a)
MgO:GGBS (1:3)	N/A	Zn (325–1950)	5–30	9–28 days	Development of immobilization from Day 7 to Day 28 after treatment	(Goodarzi and Movahedrad, 2017)
MgO:GGBS (1:8)	102	Pb (20,000)	12–18	1–28 days	Rapid immobilization from at Day 1, and then gradually developed to Day 11 and then remain relatively constant	(Nzediegwu et al., 2018)
MgO	> 1800	Pb (446–8409)	10	1 month	Effective immobilization, indication of long-term benefit	(Sanderson et al., 2015)
MgO:GGBS (1.5:8.5)	100	Pb (825–3300), Zn (825–3300)	33	7–160 days	Effective immobilization at Day 7, and remain constant at Day 28 and after	(Jin and Al-Tabbaa, 2014b)
MgO:Si-rich minerals	N/A	Zn (410), Cu (120), Pb (1700), Cr (240)	15	28 days	Effective immobilization	(Wang et al., 2019a)
MgO	N/A	Pb (736)	0.5–3.5	Simulated 100 years	Effective immobilization	(Suzuki et al., 2013)

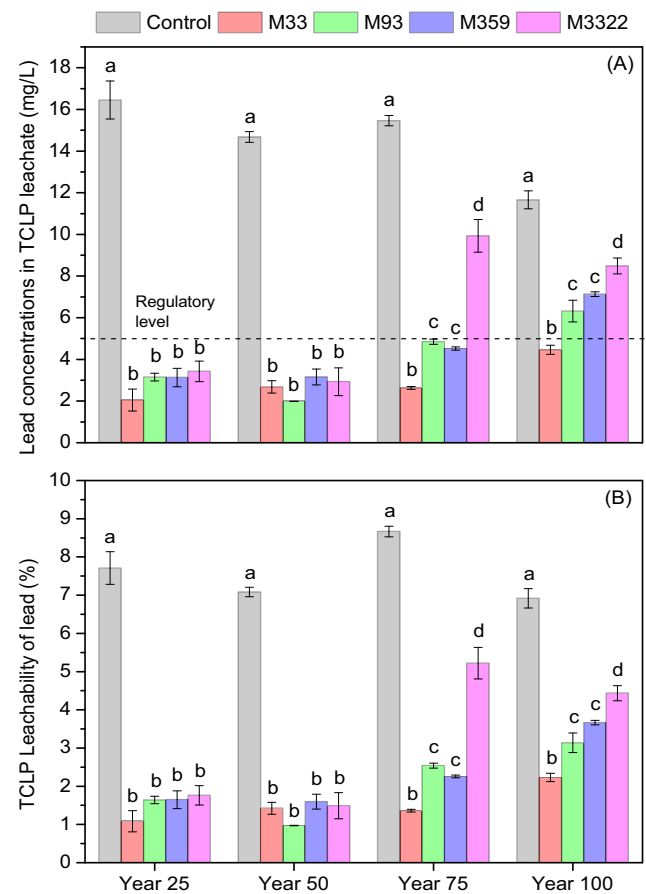


Fig. 2. TCLP leaching across 100 years of simulated ageing: (A) Pb leachate concentrations, (B) Pb leachability as a percentage of total Pb.

texture, contamination type and levels, incubation conditions, and MgO properties (e.g., reactivity, particle sizes and purity).

3.2. Long-term effectiveness

The TCLP Pb leaching results after accelerated ageing are shown in Fig. 2. It can be observed that the leachate concentrations for the untreated soil remained high (11.7–16.4 mg/L) throughout. The TCLP leaching concentrations remained lower than the regulatory level for all soils treated with MgO at simulated Year 25 and Year 50, although there was a slight increase (1.99–3.43 mg/L) over Day 49 of incubation (0.71–0.87 mg/L).

However, the M3322 treatment exceeded the regulatory level at simulated Year 75 (9.94 mg/L), suggesting 5.22% of the Pb in the soil was leachable. At simulated year 100, the leached Pb in soils treated with M93, M395, and M3322 (6.32–8.48 mg/L) all exceeded the regulatory level, with leachabilities of 3.13%–4.44%. The soil treated with M33 was the only sample whose Pb leaching remained below the regulatory level for the full 100 simulated years. As summarized in Table 3, Suzuki et al. (2013) also found that MgO could effectively stabilize Pb soil (spiked kaolinite clay) for 100 simulated years, using a H₂SO₄ solution to simulate 100-years of field ageing in one go. Other studies using MgO-based materials for heavy metal stabilization have only focused on its short-term performance.

The total Pb concentration in the soils across the simulated 100 years is shown in Fig. 3. The total Pb in the untreated soil continuously decreased from 4270 to 3370 mg/kg due to Pb leaching caused by the artificial rainwater (carbonic acid). This suggests a certain amount of Pb in the untreated soil is labile and poses a risk to the environment under long term under field conditions. In contrast, total

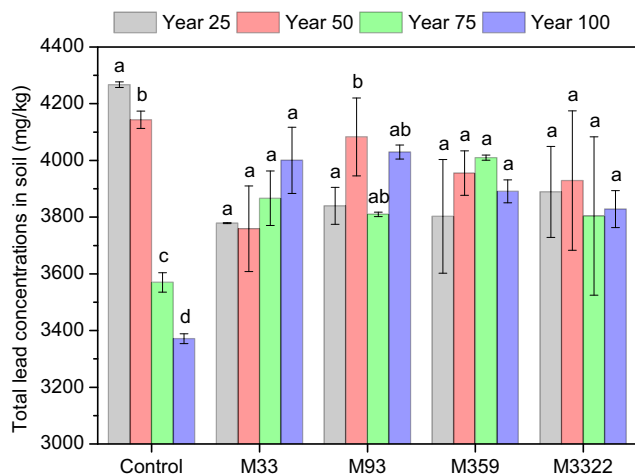


Fig. 3. Total lead concentrations in the soils with and without MgO treatments across simulated 100 years.

Pb concentrations in the samples treated with MgO did not significantly changed across the simulated 100 years, regardless of MgO reactivity. This suggests that MgO treatments can effectively inhibit the migration of Pb in the soil. However, Fig. 2A showed that the TCLP leached Pb concentrations for soil treated with M93, M359, and M3322 exceeded the regulatory level at Year 100. This suggests that although the total Pb concentrations in the treated soils were similar, the speciation of Pb may differ.

Therefore, the Pb speciation in the soils after 100 years of accelerated ageing was investigated using sequential extraction (Fig. 4 and Table 4). The exchangeable Pb (F1) in all soils was consistently negligible. It can be observed that Pb was mainly found in F2 'carbonate-bound' (13.7%) and F3 'reducible' (84.4%) fractions. The reducible fraction represents those bound to Fe/Mn oxides (Filgueiras et al., 2002). The soil contained 3.36% MnO_2 (Table 2), therefore it can be assumed that most Pb in the untreated soil would be bound to MnO_2 . The carbonate-bound fraction represents precipitated metals or Pb bound to carbonates in the soil (Filgueiras et al., 2002; Shen et al., 2017). The XRF results (Table 2) suggests the presence of CaCO_3 in the soil, which will adsorb Pb onto its surface (Filgueiras et al., 2002); the alkaline nature of the soil may have also aided the precipitation of Pb.

After MgO treatment, the carbonate-bound Pb fraction increased from 13.7% to 18.8%–26.9%, due to the increased alkalinity and buffering capacity of MgO. More importantly, the oxidizable and residual Pb fractions significantly increased from 1.84% to 23.8%–35.9% showing strong binding between Pb and MgO hydration products. The

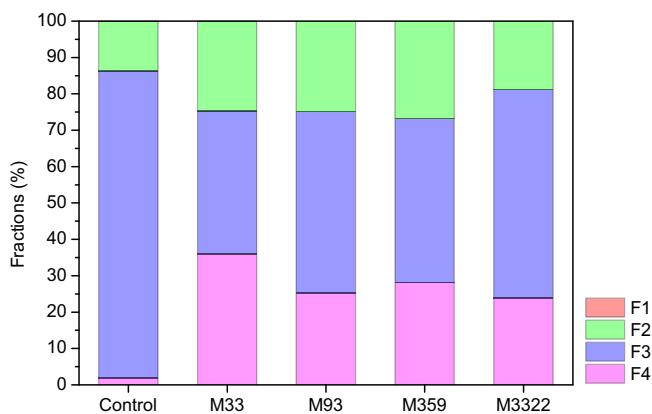


Fig. 4. Leaching behavior of lead in soils with and without MgO treatments at simulated Year 100 (F1 - exchangeable fraction, F2 - carbonate-bound fraction, F3 - reducible fraction, F4 - oxidizable and residual fractions).

residual fraction represents the most stable fraction with the lowest environmental risk. Therefore, even after simulated 100 years, the MgO treatments significantly enhanced the immobilization of Pb in the soil. The soils treated with M33 showed the highest residual Pb fraction.

3.3. Influence of MgO reactivity

It was hypothesized that MgO with higher reactivity (i.e. M33) would perform better for Pb stabilization in the short term due to its rapid dissolution and hydration rate, but it would be less effective in the long-term due to a lower buffering capacity against acid rain. The present findings reject this hypothesis. All MgO products in the investigated reactivity range (reactivity values = 33–3322 s) effectively immobilized the Pb in the soils rapidly within 1 day, and all treatments remained effective for the 49-day incubation period. The function of MgO reactivity at < 1 day is not considered valuable and was not investigated.

In the simulated long term, the M33 product with the highest reactivity revealed the best performance for Pb immobilization, being the only one to remain below the TCLP regulatory level after simulated 100 years. The soil treated with M3322 with the lowest reactivity was the first to exceed the TCLP regulatory level at simulated Year 75. This may be attributed to the highly reactive MgO having a significantly larger specific surface area (Table 1) which aids the reaction between Pb and MgO, and may also facilitate the formation of hydromagnesite-like minerals when in contact with the carbonic water. A range of hydrated magnesium carbonates (HMCs, e.g., hydromagnesite or nesquehonite) minerals can be formed in the $\text{MgO-CO}_2\text{-H}_2\text{O}$ system, and these minerals have significantly higher buffering capacity against acid dissolution than Mg(OH)_2 due to the presence of CO_3^{2-} (Hopkinson et al., 2012).

M3322 has the lowest reactivity, mainly forming Mg(OH)_2 as a hydration product with less HMCs. Therefore, Pb leaching was greater for the soil treated with M3322 than M33 after simulated 100 years. XRD was applied to identify hydromagnesite-like minerals (Fig. S2), however, no significant peaks were observed, probably due to the small amount of MgO in the soils and the low crystallinity of the HMCs.

3.4. Environmental implications and limitations

The M33 product exhibited rapid stabilizing performance and long-term effectiveness for Pb stabilization in the Pb contaminated clayey soil. Further studies are needed to determine if this would also be the case for sandy soils, however, clayey soils are typically more difficult to stabilize than sandy soils (Shen et al., 2016).

It can be observed from Fig. 5 that the pH values of the treated soils continuously decreased due to carbonization; by air in the incubation stage, and by carbonic acid dissolution in the accelerated ageing stage. After the simulated 100 years, the pH of the MgO-treated soils decreased from 10.1–10.4 to 8.46–8.54. If the accelerated ageing continued, the pH values of the soils may further decrease, and the soil treated with M33 may exceed the TCLP regulatory level for Pb eventually.

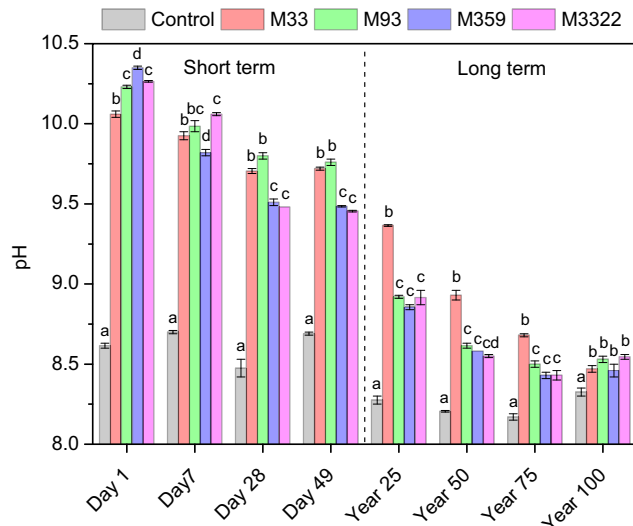
It should be noted that under field conditions, the infiltration of rainfall into a soil and its contact with soil particles depends upon the interconnected effective pore space and the hydraulic conductivity of the soil. However, in the current study, loose soil was thoroughly mixed with carbonic acid solution under continuous stirring conditions. The contact between the soil particles and the carbonic acid was much greater than it would be under field conditions, therefore, the results present here may be considered conservative. In field conditions, in addition to rainfall wash and wet and dry cycles, other environmental factors (e.g., groundwater flow, microbial activity, freezing and thawing cycle, and temperature change) may also affect the long-term effectiveness of Pb stabilization by MgO. Therefore, the accelerated ageing is suggested to couple more environmental influencing factors to

Table 4

Sequential leaching concentrations of Pb for soils with and without MgO treatments at simulated Year 100.

Step	Control		M33		M93		M359		M3322	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
F1	1.44	0.04	0.28	0.007	< LOD	N/A	< LOD	N/A	< LOD	N/A
F2	462	13.7	991	24.8	1000	24.8	1040	26.8	721	18.8
F3	2850	84.4	1570	39.3	2010	50.0	1750	45.0	2200	57.3
F4	62	1.84	1440	35.9	1020	25.2	1100	28.2	912	23.8

NOTE: LOD = limit of detection; F1 - exchangeable fraction, F2 - carbonate-bound fraction, F3 - reducible fraction, F4 - oxidizable and residual fractions.

**Fig. 5.** Variation of pH values of soils with and without MgO treatments across in the short and long terms.

perform a more comprehensive prediction.

4. Conclusions

It was observed that all four MgO products with different reactivity values effectively immobilized Pb in the contaminated clayey soil in the short term. The treated soil leachate concentrations were reduced to below the TCLP regulatory level within only 1 day, suggesting the possibility of rapid treatment of contaminated sites in practical applications.

Under simulated long-term conditions, the soil treated with M33 (the highest reactivity MgO) was the only treatment to remain below the regulatory level after 100 simulated years. Whereas the soil treated with M3322 (lowest reactivity) was the first to exceed the regulatory level at simulated Year 75. The better resistance to acid dissolution for the higher reactivity MgO treatment was attributed to the formation of hydrated magnesium carbonates that contributed to the immobilization of Pb.

In general, the M33 product showed fast stabilizing performance and long-term effectiveness. More reactive MgO products are also associated with having lower cost, and reduced energy consumption during its manufacture. This study suggests that more reactive MgO products are more suitable for the stabilization of Pb in clayey soil remediation. Further studies are warranted to examine its performance for other heavy metals and for other soil textures.

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Appendix A. Supplementary data

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